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THE SYSTEM Y_2O_3–CaO–P_2O_5

W. Szuszkiewicz

Department of Inorganic Chemistry, Faculty of Engineering and Economics, Academy of Economics, 53345 Wrocław, Poland

Abstract

The ternary system Y_2O_3–CaO–P_2O_5 has been examined by DTA, X-ray diffraction, IR and microscopic methods. Its phase diagram has been provided within the composition range YPO_4–$Ca_3(PO_4)_2$–P_2O_5. The occurrence of four mixed phosphates: $Ca_3Y(PO_4)_3$, $CaYP_3O_{10}$, $CaY(PO_3)_5$, $Ca_2Y(PO_3)_7$ has been discovered in the system. Basic X-ray data have been determined for these newly discovered compounds and several methods of their synthesis developed.

Keywords: mixed calcium–yttrium phosphates, phase equilibria

Introduction

The aim of the present study was to discover all yttrium phosphates and mixed yttrium–calcium phosphates. It was done by examining phase equilibria and determining the phase diagram of the ternary system Y_2O_3–CaO–P_2O_5. This system is surrounded by three previously known binary systems: Y_2O_3–P_2O_5 [1], Y_2O_3–CaO [2], CaO–P_2O_5 [3]. The phase equilibria of this ternary system have not been known before.

Experimental

For the examination of the system Y_2O_3–CaO–P_2O_5 the following ready for analysis, analytical grade reagents were used: Y_2O_3 99.99%, 85% H_3PO_4, $CaCO_3$, $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, $NH_4H_2PO_4$. Yttrium and calcium phosphates, as well as mixed calcium–yttrium phosphates were synthesized from these reagents. The methods of synthesis are reported in Ref. [3, 6–10].

The examinations were carried out by differential thermal analysis, on a derivatograph type 3427 (MOM, Hungary) up to 1200 and 1500°C, powder X-ray diffraction, infrared spectroscopy and microscopy in reflected light.

Horizontal resistance furnaces with molybdenum or tungsten winding were used to melt high-melting samples, under argon, within the temperature range 1500–2200°C. The furnaces had been constructed in this laboratory. The tem-

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perature was measured by means of an optical pyrometer which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$. The samples were prepared from appropriate substances which were weighed in assumed quantities, mixed, ground and pelletized. The obtained pellets were presynthesized by the reaction in the solid phase.

The phases were identified by X-ray powder diffraction on a HZG-4 diffractometer (Guinier camera) with CuK_α radiation. In order to identify phases occurring in the system, infrared spectra were measured over the range 1400–400 cm^{-1} with an IR-75 Specord spectrophotometer. The samples were prepared in the form of pellets in KBr.

The phase purity of the reagents and the phase structure of the products were studied microscopically (microsections were examined in reflected light).

Results and discussion

Figure 1 presents the phase diagram of the system Y_2O_3–CaO–P_2O_5 within the composition range YPO_4–$Ca_3(PO_4)_2$–P_2O_5, which was determined by ther-

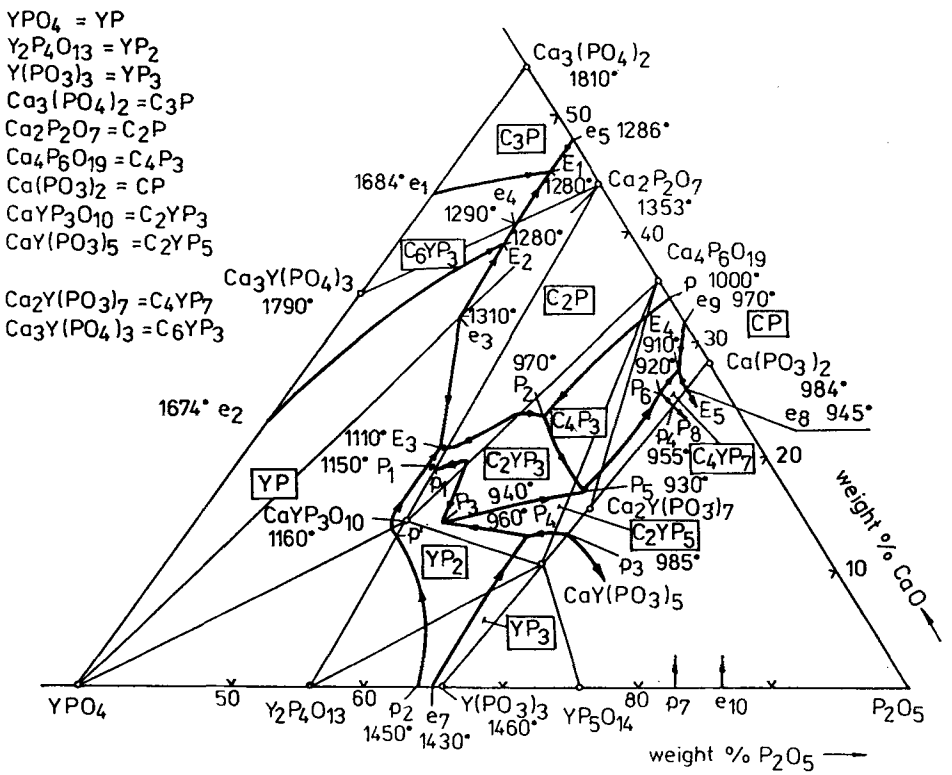

Fig. 1 Phase diagram of the system Y_2O_3–CaO–P_2O_5

mal analysis, X-ray and microscopy. Nine binary compounds and four ternary compounds occur in the region under investigation. All compounds crystallize from the liquid phase. Each of them has a particular primary crystallization field, which is shown in Fig. 1. The primary crystallization fields of these compounds are separated by eutectic or peritectic curves. Five ternary eutectics and six ternary peritectics occur within the composition range YPO_4–$Ca_3(PO_4)_2$–P_2O_5. The temperatures of the beginning of crystallization cover a large range, from approx. 700°C with samples rich in P_2O_5 to over 2000°C with samples rich in Y_2O_3.

The examined composition range can be divided into eleven partial ternary systems. In most of these systems the phase equilibria are complex and often correlated. Therefore they should be discussed together. For that reason all the composition range under investigation was divided into four regions: 1) the partial

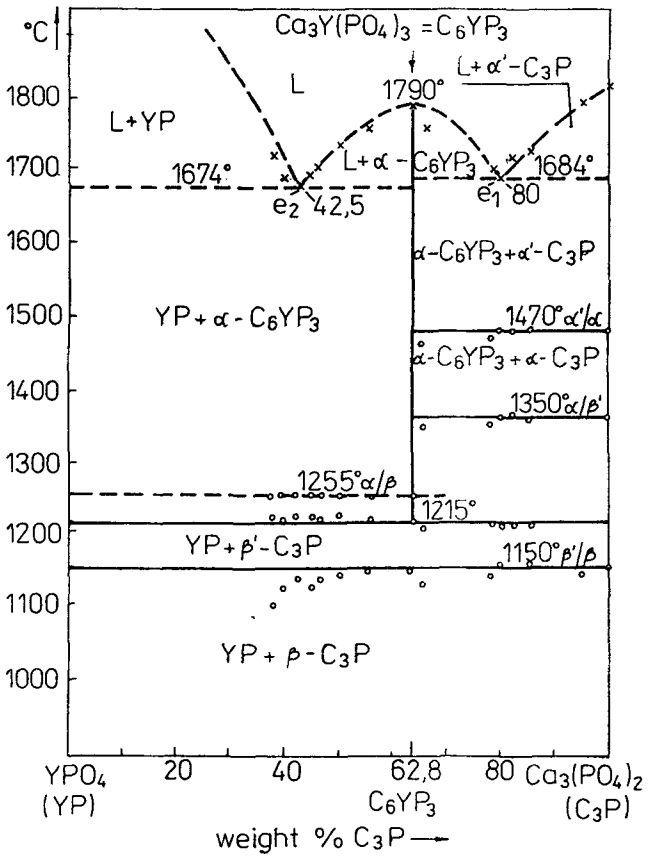

Fig. 2 Phase diagram of the system YPO_4–$Ca_3(PO_4)_2$. o, thermal analysis; x, optical

system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ [4], 2) the partial system YPO_4–$Ca_2P_2O_7$–$Y_2P_4O_{13}$ [5], 3) the partial system $Y_2P_4O_{13}$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$Y(PO_3)_3$ [6], 4) the partial system $Y(PO_3)_3$–$Ca(PO_3)_2$–P_2O_5 [7].

The binary system YPO_4–$Ca_3(PO_4)_2$ [8] is of great importance in the partial system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$. The phase diagram of this binary system is presented in Fig. 2. The mixed orthophosphate with the formula $Ca_3Y(PO_4)_3$ occurs in the system. It was discovered that this compound melts congruently at 1790°C and is stable only up to 1215°C. It decompose into YPO_4 and β–$Ca_3(PO_4)_2$ in the solid phase, at 1215°C. Phosphate $Ca_3Y(PO_4)_3$ shows a polymorphic transition at 1255°C. On the basis of the powder X-ray analysis, the structure of the low-temperature modification β–$Ca_3Y(PO_4)_3$ was delivered (regular system a=9.835Å, V=951.3 Å^3). The methods of synthesing $Ca_3Y(PO_4)_3$ are reported in Ref. [9].

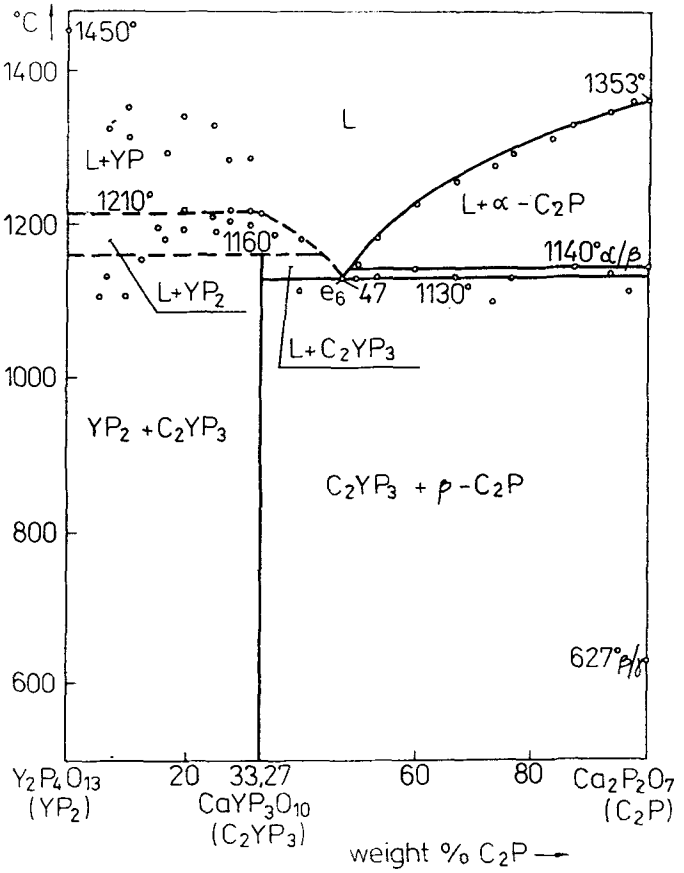

Fig. 3 Phase diagram of the system $Y_2P_4O_{13}$–$Ca_2P_2O_7$

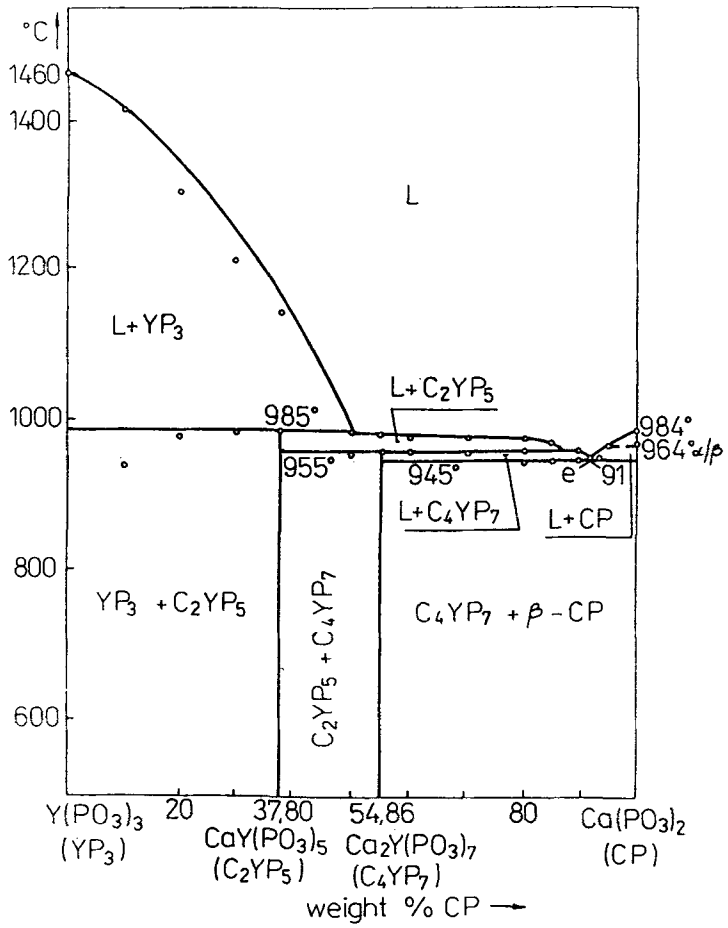

Fig. 4 Phase diagram of the system $Y(PO_3)_3$–$Ca(PO_3)_2$

In the partial system YPO_4–$Ca_2P_2O_7$ –$Y_2P_4O_{13}$ the binary system $Y_2P_4O_{13}$–$Ca_2P_2O_7$ is of primary importance. Its phase diagram is shown in Fig. 3. The mixed triphosphate with the formula $CaYP_3O_{10}$ occurs at this section. It is difficult to determine the temperature range of $CaYP_3O_{10}$ stability precisely and univocally as it changes according to the thermal treatment that was used. It was assumed that this phosphate decomposes peritectically at approx. 1160°C. $CaYP_3O_{10}$ is stable up to room temperature and has no polymorphic transitions. It can be obtained by several methods. Phosphate $CaYP_3O_{10}$ influences also the phase equilibria in the other partial system, i.e. $Y_2P_4O_{13}$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$Y(PO_3)_3$, forming two sections with it. In the partial system mentioned above and in the partial system $Y(PO_3)_3$–$Ca(PO_3)_2$–P_2O_5 , the binary system $Y(PO_3)_3$–

$Ca(PO_3)_2$ [10] is worthy to notice. The phase equilibria occurring in this system are presented in Fig. 4. Two mixed meta-phosphates are formed at the 1:1 and 1:2 molar ratios of the initial metaphosphates in the system $Y(PO_3)_3$–$Ca(PO_3)_2$. They were given the formulas $CaY(PO_3)_5$ and $Ca_2Y(PO_3)_7$. These compounds decompose peritectically at 985 and 955°C respectively. They are stable up to room temperature and do not show any polymorphic modifications. Basic X-ray data were given for both these mixed metaphosphates.

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Zusammenfassung — Mittels DTA, Röntgendiffraktion, IR-Spektroskopie und mikroskopischen Methoden wurde das ternäre System Y_2O_3–CaO–P_2O_5 untersucht. Das Phasendiagramm wurde für das Zusammensetzungsintervall YPO_4–$Ca_3(PO_4)_2$–P_2O_5 erstellt. In diesem System konnte die Existenz von vier Mischphosphaten entdeckt werden: $Ca_3Y(PO_4)_3$, $CaYP_3O_{10}$, $CaY(PO_3)_5$ und $Ca_2Y(PO_3)_7$. Für diese neuentdeckten Verbindungen wurden grundlegende Röntgendaten ermittelt und einige Methoden zu ihrer Synthese entwickelt.